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(54) **Acid microemulsion composition.**

(57) **An acidic thickened microemulsion composition which contains alpha hydroxy aliphatic acids and is effective in removing soap scum.**

**Field of Invention**

This invention relates to a cleaner for hard surfaces, such as bathtubs, sinks, tiles, porcelain and enamelware, which removes soap scum, lime scale and grease from such surfaces without harming them. More particularly, the invention relates to an acidic microemulsion that can be sprayed onto the surface to be cleaned, and wiped off without usual rinsing and still leave the cleaned surface bright and shiny. The invention also relates to a method for using such compositions.

**Background of Invention**

Hard surface cleaners, such as bathroom cleaners and scouring cleansers, have been known for many years. Scouring cleansers normally include a soap or synthetic organic detergent or surface active agent and an abrasive. Such products can scratch relatively soft surfaces and can eventually cause them to appear dull. These products are often ineffective to remove lime scale (usually encrusted calcium and magnesium carbonates) in normal use. Because lime scale can be removed by chemical reactions with acidic media various acidic cleaners have been produced and have met with various degrees of success. In some instances such cleaners have been failures because the acid employed was too strong and damaged the surfaces being cleaned. At other times, the acidic component of the cleaner reacted objectionably with other components of the product which adversely affected the detergent or perfume. Some cleaners required rinsing afterward to avoid leaving objectionable deposits on the cleaned surfaces. As a result of research performed in efforts to overcome the mentioned disadvantages there has recently been made an improved liquid cleaning composition in stable microemulsion form which is an effective cleaner to remove soap scum, lime scale and greasy soils from hard surfaces, such as bathroom surfaces and which does not require rinsing after use. Such a product is described in U.S. patent application S.N. 120,250 for Stable Microemulsion Cleaning Composition filed November 12, 1987 by Loth, Blanvalet and Valenge, which application is hereby incorporated by reference. In particular, Example 3 of that application discloses an acidic, clear, oil-in-water microemulsion which is therein described as being successfully employed to clean shower wall tiles of lime scale and soap scum that had adhered to them. Such cleaning was effected by applying the cleaner to the walls followed by wiping or minimal rinsing after which the walls were allowed to dry to a good shine.

The described microemulsion cleaner of that patent application is effective in removing lime scale and soap scum from hard surfaces and is easy to use, but it has been found that its mixture of acidic agents (succinic, glutaric and adipic acids) could damage the surfaces of some hard fixtures, such as those of materials which are not acid resistant. One of such materials is an enamel that has been extensively employed in Europe as a coating for bathtubs, herein referred to as European enamel. It has been described as zirconium white enamel or zirconium white powder enamel and has the advantage of being resistant to detergents, which makes it suitable for use on tubs, sinks, shower tiles and bathroom enamelware. However, such enamel is sensitive to acids and is severely damaged by use of the microemulsion acidic cleaner based on the three organic carboxylic acids previously mentioned.

That problem was been solved by EPO patent 0336878A2. In that case additional acidic materials are incorporated in the cleaner with the organic acids and rather than exacerbating the problem, they prevent harm to such European enamel surfaces by such organic acids. Also, a mixture of such additional acids, phosphonic and phosphoric acids surprisingly further improves the safety of the aqueous cleaner for use on such European enamel surfaces and decreases the cost of the cleaner.

The instant compositions of present invention allow the cleaning of European enamel surfaces, as well as any other acid resistant surfaces of bathtubs and other bathroom surfaces. The product can be used on various other materials that are especially susceptible to attack by acidic media, such as marble. The instant compositions employ alpha-hydroxy aliphatic acids in place of the mixture of succinic, glutaric and adipic acids previously used in the acidic microemulsion. The instant compositions which employ the alpha hydroxy aliphatic acids are less detrimental to European enamel or other acid susceptible surfaces such as marble than the mixture of succinic, glutaric and adipic. Additionally, it is contemplated that the instant inventions can be thickened by a xanthan gum such as described in copending U.S. Serial No. 07/950,370 filed September 1992.

**Summary of the Invention**

In accordance with the present invention, an acidic aqueous cleaner for bathtubs and other hard surfaced items, which are acid resistant or are of zirconium white enamel wherein the cleaner has a pH in the range of 1 to 4 and the cleaner removes lime scale, soap scum and greasy soil from surfaces of such items without damaging such surfaces, comprises: a deterative proportion of at least one synthetic organic detergent which is

capable of removing greasy soil from such surfaces; a lime scale and soap scum removing proportion of an alpha-hydroxy aliphatic acid(s) having 2 to 6 preferably 3 to 5 carbon atoms; an aminoalkylenephosphonic acid in such proportion as to prevent damage to zirconium white enamel surfaces of items to be cleaned by the alpha-hydroxy aliphatic acid; phosphoric acid and an aqueous medium for the detergent, alpha hydroxy aliphatic acid, phosphoric acid and aminoalkylenephosphonic acid.

### Detailed Description of the Invention

The present thickened, acidic microemulsion compositions preferably comprise approximately by weight:

- (a) 1 to 9 percent of an anionic surfactant such as a C<sub>14-17</sub> alkali metal or ammonium sulfonate; C<sub>8</sub>-C<sub>18</sub> alkali metal or ammonium alkyl sulfate or a C<sub>8</sub>-C<sub>18</sub> alkali metal or ammonium ethoxylated alkyl ether sulfate;
- (b) 0 to 5 percent of a nonionic surfactant such as a C<sub>13-15</sub> Fatty Alcohol EO 7:1/PO 4:1;
- (c) 0 to 0.7 percent of a preservative such as an alkali metal benzoate such as sodium benzoate;
- (d) 0 to 1.0 percent of a xanthan gum thickener having a molecular weight of about 1,000,000 to 10,000,000 such as Kelzan T sold by Merck & Co.;
- (e) 0 to 0.3 percent of an alkali metal hydroxide;
- (f) 0 to 1.0 % of phosphoric acid, more preferably 0.05 to 1.0 percent;
- (g) 0 to 0.5 percent of an amino trimethyl phosphonic acid, more preferably 0.01 to 0.3 percent;
- (h) 0 to 0.1 percent of a dye;
- (i) 0 to 2.0 percent of a perfume;
- (j) 2 to 9 percent of at least one alpha hydroxy aliphatic acid having 2 to about 6 carbon atoms; and
- (k) balance being water, wherein the composition has a pH of about 1 to about 4, more preferably about 2.7 to about 3.3 and a Brookfield viscosity of about 5 to 1,000 cps, more preferably about 30 to about 600 cps at R.T. using a #2 spindle and 50 rpm.

In the present compositions, the synthetic organic detergent may be any suitable anionic, nonionic, amphoteric, ampholytic, zwitterionic or cationic detergent or mixture thereof, but anionic and nonionic detergents are preferred as well as mixtures thereof.

The nonionic surfactant that can be employed in the present liquid detergent composition is present in amounts of about 0 to 5%, preferably 0.5 to 4.5%, most preferably 1 to 4%, by weight of the composition and provides superior performance in the removal of soil.

The water soluble nonionic surfactants utilized in this invention are preferably commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates on primary alkanols, such as Plurafacs (BASF) and condensates of ethylene oxide with sorbitan fatty acid esters such as the Tweens (ICI). The nonionic synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic detergent. Further, the length of the polyethenoxy hydrophobic and hydrophilic elements.

The nonionic detergent class includes the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide (EO), tridecanol condensed with about 6 to 10 moles of EO, myristyl alcohol condensed with about 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of EO per mole of total alcohol or about 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing about 9-15 carbon atoms, such as C<sub>9</sub>-C<sub>11</sub> alkanol condensed with 8 moles of ethylene oxide (Neodol 91-8), C<sub>12-13</sub> alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C<sub>12-15</sub> alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C<sub>14-15</sub> alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of about 8 to 15 and give good O/W (oil in water) emulsification, whereas ethoxamers with HLB values below 8 contain less than 5 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of

the foregoing type are C<sub>11</sub>-C<sub>15</sub> secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic detergents include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight- or branched chain alkyl group with about 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl condensed with about 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with about 12 moles of EO per mole of phenol, dinonyl phenol condensed with about 15 moles of EO per mole of phenol and di-isooctylphenol condensed with about 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

Also among the satisfactory nonionic detergents are the water-soluble condensation products of a C<sub>8</sub>-C<sub>20</sub> alkanol with a heteric mixture of ethylene oxide and propylene oxide wherein the weight ratio of ethylene oxide to propylene oxide is from 2.5:1 to 4:1, preferably 2.8:1 to 3.3:1, with the total of the ethylene oxide and propylene oxide including the terminal ethanol or propanol group) being from 60 to 85%, preferably 30 to 80%, by weight. Such detergents are commercially available from BASF-Wyandotte and a particularly preferred detergent is a C<sub>10</sub>-C<sub>18</sub> alkanol condensate with ethylene oxide and propylene oxide, the weight ratio of ethylene oxide to propylene oxide being 3:1 and the total alkoxy content being about 75% by weight.

Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-C<sub>10</sub>-C<sub>20</sub> alkanolic acid esters having a HLB of 8 to 15 also may be employed as the nonionic detergent ingredient in the described shampoo. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan trioleate and polyoxyethylene (20) sorbitan tristearate.

Other suitable water-soluble nonionic detergents which are less preferred are marketed under the trade name "Pluronic". These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is of the order of 950 to 4000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals to the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. The molecular weight of the block polymers varies from 1,000 to 15,000 and the polyethylene oxide content may comprise 20% to 80% by weight. Preferably, these surfactants will be in liquid form and satisfactory surfactants are available as grades L62 and L64.

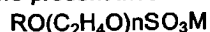
The anionic surfactant, used in the microemulsion composition, constitutes about 1% to 9%, preferably 2% to 8%, most preferably 2% to 7%, by weight.

The anionic surfactants which may be used in the instant microemulsion detergent of the invention are water soluble such as triethanolamine salt and include the sodium, potassium, ammonium and ethanolammonium salts of C<sub>8</sub>-C<sub>18</sub> alkyl sulfates such as lauryl sulfate, myristyl sulfate and the like; C<sub>8</sub>-C<sub>18</sub> ethoxylated alkyl ether sulfates; linear C<sub>8</sub>-C<sub>18</sub> alkyl benzene sulfonates; C<sub>10</sub>-C<sub>20</sub> paraffin sulfonates; alpha olefin sulfonates containing about 10-24 carbon atoms; C<sub>8</sub>-C<sub>18</sub> alkyl sulfoacetates; C<sub>8</sub>-C<sub>18</sub> alkyl sulfosuccinate esters; C<sub>8</sub>-C<sub>18</sub> acyl isethionates; and C<sub>8</sub>-C<sub>18</sub> acyl taurates. Preferred anionic surfactants are the water soluble alkyl sulfates.

The paraffin sulfonates may be monosulfonates or disulfonates and usually are mixtures thereof, obtained by sulfonating paraffins of 10 to 20 carbon atoms. Preferred paraffin sulfonates are those of C<sub>12</sub>-C<sub>18</sub> carbon atoms chains, and more preferably they are of C<sub>14</sub>-C<sub>17</sub> chains. Paraffin sulfonates that have the sulfonate group(s) distributed along the paraffin chain are described in U.S. Patents 2,503,280; 2,507,088; 3,260,744; and 3,372,188; and also in German Patent 735,096. Such compounds may be made to specifications and desirably the content of paraffin sulfonates outside the C<sub>14</sub>-C<sub>17</sub> range will be minor and will be minimized, as will be any contents of di- or poly-sulfonates.

Examples of suitable other sulfonated anionic detergents are the well known higher alkyl mononuclear aromatic sulfonates, such as the higher alkylbenzene sulfonates containing 9 to 18 or preferably 9 or 10 to 15 or 16 carbon atoms in the higher alkyl group in a straight or branched chain, or C<sub>8</sub>-C<sub>15</sub> alkyl toluene sulfonates. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher content of 3-phenyl (or higher isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly at the 3 or higher (for example 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

The higher alkyl ether sulfates used in the present invention are represented by the formula:



in which R is a primary or secondary alkyl group that may be straight or branched having from 10 to 18 carbon atoms, preferably 12 to 15, especially 12 to 14, and most preferably 12 to 13 carbon atoms. M is an alkali metal

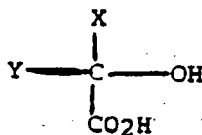
or ammonium cation and n is a number from 1 to 10, preferably 1 to 6, especially 2 or 3. These detergents are produced by sulfating the corresponding ether alcohol and then neutralizing the resulting sulfuric acid ester thereof. The sodium and ammonium salts of the ether sulfates are especially preferred.

The alkyl sulfate anionic detergent compounds which are useful in the present invention have from 6 to 18 carbon atoms in the alkyl group and can be represented by the following general formula:



in which  $R^2$  is straight or branched chain alkyl of from 6 to 8, especially from 8 to 14 carbon atom chain length and M is an alkali metal or ammonium cation, especially sodium. Straight chain alkyl groups are preferred.

The active acidic component of the acidic emulsions is an alpha hydroxy aliphatic acid which is strong enough to lower the pH of the microemulsion to be in the range of one to four. Various such carboxylic acids can perform this function but those which have been found effectively to remove soap scum and lime scale from bathroom surfaces best, while still not destabilizing the emulsion, are alpha hydroxy aliphatic acids having the structure:

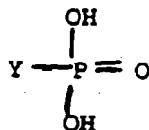


wherein Y is selected from the group consisting of hydroxy or a  $COOH$  group and X is  $(CH_2)_nW$ , wherein W is selected from the group consisting of  $CH_3$  or  $COOH$  and n is 0, 1, or 2. Preferred alpha hydroxy aliphatic acids are citric acid, lactic acid and malic acid, wherein a mixture of lactic acid and malic acid is preferred, wherein the weight ratio of lactic acid to malic acid is preferred to be about 5:1 to about 1:1, more preferably about 4:1 to about 1:1. The at least one alpha hydroxy aliphatic acid is incorporated in the composition in an amount of about 2 to about 9 wt. %, more preferably about 2 to about 7 wt. %.

The alpha hydroxy aliphatic acid, after being incorporated in the acidic emulsion, may be partially neutralized to produce the desired pH in the emulsion, for greatest functional effectiveness, with safety.

Phosphoric acid is one of the additional acids that helps to protect acid-sensitive surfaces being cleaned with the present emulsion cleaner. Being a tribasic acid, it too may be partially neutralized to obtain an emulsion pH in the desired range. For example, it may be partially neutralized to the biphosphate, e.g.,  $NaH_2PO_4$ , or  $NH_4H_2PO_4$ .

Phosphonic acid, the other of the two additional acids for protecting acid-sensitive surfaces from the dissolving action of the dicarboxylic acids of the present thickened emulsions, apparently exists only theoretically, but its derivatives are stable and are useful in the practice of the present invention. Such are considered to be phosphonic acids as that term is used in this specification. The phosphonic acids are of the structure.



wherein Y is any suitable substituent, but preferably Y is alkylamino or N-substituted alkylamino. For example, a preferred phosphonic acid component of the present thickened acidic emulsions is aminotri (methylenephosphonic) acid which is of the formula  $N(CH_2PH_xO_3)$ . Among other useful phosphonic acids are ethylene diamine tetra-(methylenephosphonic) acid, hexamethylenediamine tetra-(methylenephosphonic) acid, and diethylenetriamine penta-(methylenephosphonic) acid. Such class of compounds may be described as aminoalkylenephosphonic acids containing in the range of 1 to 3 amino nitrogen, 3 or 4 lower alkylenephosphonic acid groups in which the lower alkylene is of 1 or 2 carbon atoms, and 0 to 2 alkylene groups of 2 to 6 carbon atoms each, which alkylene(s) is/are present and join amino nitrogen when a plurality of such amino nitrogen is present in the aminoalkylenephosphonic acid. It has been found that such aminoalkylenephosphonic acids, which also may be partially neutralized at the desired pH of the microemulsion cleaner, are of desired stabilizing and protecting effect in the invented cleaner, especially when present with phosphoric acid, preventing harmful attacks on European enamel surfaces by the alpha hydroxy aliphatic components of the cleaner.

The thickener which is optionally used in the acidic microemulsion is a xanthan gum called Kelzan T sold by Merck & Co. The xanthan gum is an exocellular heteropolysaccharide having a molecular weight of about

1,000,000 to 10,000,000 and is used in a concentration of 0 to about 1.0 weight percent, more preferably about 0.1 to about 0.7 weight percent, and most preferably 0.2 to 0.6 weight percent. When used at these concentration levels, the composition retains its microemulsion characteristics in that the essential micellar aggregates are maintained. The composition is still sprayable and will cling nicely to a vertical wall. Additionally, the compositions having the xanthan gum incorporated therein are shear thinning which means that the composition can be easily removed from the surface being cleaned without much mechanical action. Other cellulose, hydroxypropyl cellulose, polyacrylamides and poly vinyl alcohol will create shear thickening compositions.

The water that is used in making the present microemulsions may be tap water but is preferably of low hardness, normally being less than 150 parts per million (p.p.m.) of hardness. Still, useful cleaners can be made from tap waters that are higher in hardness, up to 3000 p.p.m. Most preferably the water employed will be distilled or deionized water, in which the content of hardness ions is less than 25 p.p.m.

Various other components may desirably be present in the invented cleaners, including preservatives such as sodium benzoate, antioxidants or corrosion inhibitors, cosolvents, cosurfactant, multivalent metal ions, perfumes, colorants and terpenes (and terpeneols), but various other adjuvants conventionally employed in liquid detergents and hard surface cleaners may also be present, provided that they do not interfere with the cleaning and scum-and scale-removal functions of the cleaner. Of the various adjuvants (which are so identified because they are not necessary for the production of an operative cleaner, although they may be very desirable components of the cleaner) the most important are considered to be the perfumes, which, with terpenes, terpenes and hydrocarbons (which may be substituted for the perfumes or added to them) function as especially effective solvents for greasy soils on hard surfaces being cleaned, and form the dispersed phases of oil-in-water (o/w) microemulsions. Also of functional importance are the co-surfactant and polyvalent metal ions, with the former helping to stabilize the microemulsion and the latter adding in improving detergency, especially for more dilute cleaners, and when the polyvalent salts of the anionic detergent are employed affording more effective detergents against the greasy soil encountered in use.

The various perfumes that have been found to be useful in forming the dispersed phase of the thickened acidic microemulsion cleaners may be those normally employed in cleaning products and preferably are normally in liquid state. They include esters, ethers, aldehydes, alcohols and alkanes employed in perfumery but of most importance are the essential oils that are high in terpene content. It appears that the terpenes (and terpeneols) coact with the deterative components of microemulsions to improve detergency of the invented compositions, in addition to forming the stable dispersed phase of the microemulsions. In the present invention it has been found that especially when a piney perfume is being employed, one can decrease the proportion of comparatively expensive such perfume and can compensate for it with alpha-terpineol, and in some instances with other terpenes. For example, for every 1% of perfume one can substitute from 60 to 90% of it, w.g., about 80%, with alpha-terpineol, and obtain essentially the same piney scent, with good cleaning and microemulsion stability. Similarly, terpenes and other terpene-like compounds and derivatives may be employed, but alpha-terpineol is considered to be the best.

The polyvalent metal ion present in the invented cleaners may be any suitable ion including, but not limited to, magnesium (usually preferred) aluminum, copper, nickel, iron or calcium. The ion or mixture thereof may be added in any suitable form, sometimes as an oxide or hydroxide, but usually as a water soluble salt. It appears that the polyvalent metal ion reacts with the anion of the anionic detergent (or replaces the detergent cation, or makes an equivalent solution in the emulsion), which improves detergency and generally improves other properties of the product, too. If the polyvalent metal ion reacts with the detergent anion to form an insoluble product such polyvalent ion should be avoided. For example, calcium reacts with paraffin sulfonate anion to form an insoluble salt, so calcium ions, such as might be obtained from calcium chloride, will be omitted from any microemulsion cleaners of this invention that contain paraffin sulfonate detergent. Similarly, those polyvalent ions or other components of the invented compositions that will react adversely with other components will also be omitted. As was mentioned previously, the polyvalent metal ion will preferably be magnesium, and such will be added to the other emulsion components as a water soluble salt. A preferred such salt is magnesium sulfate, usually employed as its heptahydrate (Epsom salts), but other hydrates thereof or the anhydride may be used too. Generally, the sulfates of the polyvalent metals will be used because the sulfate anion thereof is also the anion of some of the anionic detergents and is found in some such detergents as a byproduct of neutralization.

The cosurfactant component(s) of the acidic cleaners reduce the interfacial tension or surface tension between the lipophilic droplets and the continuous aqueous medium to a value that is often close to  $10^{-3}$  dynes/cm., which results in spontaneous disintegrations of the dispersed phase globules until they become so small as to be invisible to the human eye forming a clear microemulsion. In such a microemulsion the surface area of the dispersed phase increases greatly and its solvent power and grease removing capability are also increased, so that the acidic microemulsion is significantly more effective as a cleaner for removing greasy

soil than when the dispersed phase globules are of ordinary emulsion size. Among the cosurfactants that are useful in the invented cleaners are: water soluble lower alkanols of 2 to 4 carbon atoms per molecule (sometimes preferably 3 or 4); polypropylene glycols of 2 to 18 propoxy units; monoalkyl lower glycol ethers of the formula  $RO(X)_nH$ , wherein R is  $C_{1-4}$  alkyl, X is  $CH_2CH_2CH_2O$  or  $CH(CH_3)CH_2O$ , and n is from 1 to 4; monoalkyl esters of the formula  $R^1$  is  $C_{2-4}$  acyl and X and n are as immediately previously described; aryl substituted alkanols of 1 to 4 carbon atoms; propylene carbonate; alpha hydroxy aliphatic acids of 2 to 6 carbon atoms such as mono- di- and tri hydroxy substituted aliphatic mono- di- and tricarboxylic acids of 2 to 6 carbon atoms; lower alkyl mono- di- and triesters of phosphoric acid wherein the lower alkyl is of 1 to 4 carbon atoms; and mixtures thereof.

It also obvious that other previously identified cosurfactants can be used in combination with the alpha hydroxy aliphatic acids which function as cosurfactants. These non acid cosurfactants will usually be used in conjunction with the alpha hydroxy aliphatic acid cosurfactants in an amount of about 0.1 to about 5 wt. %, more preferably about 0.5 to about 4.0 wt. % depending upon the concentration of the alpha hydroxy aliphatic acid cosurfactant.

Representative of such cosurfactants are lactic, malic and citric acids, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether and diethylene glycol mono-isobutyl ether, which are considered to be the most effective.

From the foregoing discussion of useful cosurfactants in the present cleaners it is apparent that malic, lactic and citric acids, and a mixture of such components are useful for lowering the pH of the product so that it removes soap scum and lime scale easily from surfaces to be cleaned, and at the same time they function as cosurfactants, improving the appearance of the product and making it more effective for removing grease from such surfaces. Similar dual effects may be obtained by use of other of the named acidic materials that have cosurfactant activities in the described cleaners.

In the invented cleaners it is important that the proportions of the components are in certain ranges so that the product may be most effective in removing greasy soils, lime scale and soap scum, and other deposits from the hard surfaces subjected to treatment, and so as to protect such surfaces during such treatment. As was previously referred to the detergent should be present in detergent proportion, sufficient to remove greasy and oily soils; the proportion(s) of the alpha hydroxy aliphatic acid(s) should be sufficient to remove soap scum and lime scale; the phosphonic acid or phosphoric and phosphonic acids mixture should be enough to prevent damage of acid sensitive surfaces by the alpha hydroxy aliphatic acid(s); and the aqueous medium should be a solvent and suspending medium for the required components and for any adjuvants that may be present, too. Normally, such percentages of components will be by weight 0 to 1.0% of xanthan gum, 1 to 9% of synthetic anionic organic detergent(s), 0 to 5% of synthetic organic nonionic detergent(s), 2 to 9% of alpha hydroxy aliphatic acids, 0.05 to .6% of phosphoric acid or mono-salt thereof and 0.005 to 2% of phosphonic acid(s), 0 to 0.6% aminoalkylenephosphonic acid(s), or mono-phosphonic salt(s) thereof; and the balance being water and adjuvant's if any are present. Of the alpha hydroxy aliphatic acids it is preferred that a mixture of lactic and malic acids be employed.

The ratio of the alpha hydroxy aliphatic acid to the aminoalkylenephosphonic acid in the instant composition is about 5:1 to about 250:1, more preferably about 2:1 to about 10:1 and the ratio of the alpha hydroxy aliphatic acid to the phosphoric acid is about 5:2 to 25:1.

Usually there will be present in the cleaner, especially when an anionic surfactant is present 0.05 to 5%, and preferably 0.1 to 3.0% of polyvalent ion, preferably magnesium or aluminum, and more preferably magnesium. Also, the percentage of perfume will normally be in the 0.2 to 2% range, preferably being in the 0.5 to 1.5% range of which perfume at least 0.1% is terpene or terpineol. The terpineol is alpha-terpineol and is preferably added to allow a reduction in the amount of perfume, with the total perfume (including the alpha-terpineol) being 50 to 90% of terpineol, preferably about 80% thereof.

The pH of the various preferred microemulsion cleaners is usually 1 to 4, preferably 1.5 to 3.5 e.g. 3. The water content of the microemulsions will usually be in the range of about 75 to 90%, preferably about 80 to 85% and the adjuvant content will be from 0 to 5%, usually about 1 to 3%. If the pH is not in the desired range it will usually be adjusted with either sodium hydroxide or suitable acid, e.g. sulfuric acid, solution, but normally the pH will be raised, not lowered, and it if is to be lowered more of the alpha hydroxy acid mixture can be used, instead.

The liquid cleaners can be manufactured by merely mixing of the various components thereof, with orders or additions not being critical. However, it is desirable for the optionally added xanthan gum to be first mixed with the water, various water soluble components to be mixed together into the xanthan gum solution, the oil soluble components to be mixed together in a separate operation, and the two mixes to be admixed, with the oil soluble portion being added to the water soluble portion (in the water) with stirring or other agitation.

In some instances, such procedure may be varied to prevent any undesirable reactions between components. For example, one would not add concentrated phosphoric acid directly to magnesium sulfate or to a dye, but such additions would be of aqueous solutions, preferably dilute of the components.

The cleaner may desirably be packed in manually operated spray dispensing containers, which are usually and preferably made of synthetic organic polymeric plastic material, such as polyethylene, polypropylene or polyvinyl chloride (PVC). Such containers also preferably include nylon or other non-reactive plastic closure, spray nozzle, dip tube and associated dispenser parts, and the resulting packaged cleaner is ideally suited for use in "spray and wipe" applications. However, in some instances, as when lime scale and soap scum deposits are heavy, the cleaner may be left on until it has dissolved or loosened the deposit(s) and may then be wiped off, or may be rinsed off, or multiple applications may be made, followed by multiple removals, until the deposits are gone.

The following examples illustrate but do not limit the invention. All parts, proportions and percentages in the examples, the specification and claims are by weight and all temperatures are in °C unless otherwise indicated.

#### Example 1

| Component                             | % (by weight) |         |         |
|---------------------------------------|---------------|---------|---------|
|                                       | A             | B       | C       |
| Sodium lauryl sulfate                 | 4.00          | 3.0     | 4.0     |
| C <sub>13-15</sub> Na Benzoate        | 0.30          | 0.3     | 0.3     |
| Magnesium sulfate heptahydrate        | 1.50          | 1.5     | 1.5     |
| Malic acid                            | 2.0           | 2.0     | --      |
| Lactic acid                           | 2.0           | 3.0     | --      |
| Citric acid                           | --            | --      | 4.0     |
| Aminotri                              | 0.25          | 0.25    | 0.25    |
| Methylphosphonic Acid Phosphoric Acid | 0.425         | 0.425   | 0.425   |
| Perfume (contains about 40% terpenes) | 0.8           | 0.8     | 0.8     |
| Dye                                   | 0.002         | 0.002   | 0.002   |
| Water                                 | Balance       | Balance | Balance |
| pH                                    | 3.0           | 3.0     | 3.0     |
| Viscosity Brookfield                  | 10            | 10      | 10      |
| RT, #2 spindle                        |               |         |         |
| Sorpins (cps)                         | Balance       |         |         |
|                                       | 100.00        |         |         |

The microemulsion cleaner is made by dissolving the optional xanthan gum and benzoates and then dissolving the detergent in the water, after which the rest of the water soluble materials are added to the detergent solution, with stirring, except for the perfume and the adjusting agent (sodium hydroxide solution). The pH is adjusted to 3.0 and then the perfume is stirred into the aqueous solution, instantaneously generating the desired microemulsion, which is clear blue.

The acid cleaner is packed in polyethylene squeeze bottles equipped with polypropylene spray nozzles which are adjustable to closed spray and stream positions. In use the microemulsion is sprayed onto "bathtub ring" on a bathtub, which also includes lime scale, in addition to soap scum and greasy soil. The rate of application is about 5 ml. per 5 meters of ring (which is about 3 cm. wide). After application and a wait of about two



minutes the ring is wiped off with a sponge and is sponged off with water, it is found that the greasy soil, soap scum, and even the lime scale, have been removed effectively. In those cases where the lime scale is particularly thick or adherent a second application may be desirable, but that is not considered to be the norm.

The tub surface may be rinsed because it is so easy to rinse a bathtub (or a shower) but such rinsing is not necessary.

Sometimes dry wiping will be sufficient but if it is desired to remove any acidic residue the surface may be sponged with water or wiped with a wet cloth but in such case it is not necessary to use more than ten times the weight of cleaner applied. In other words, the surface does not need to be thoroughly doused or rinsed with water, and it still will be clean and shiny (providing that it was originally shiny). In other uses of the cleaner, it may be employed to clean shower tiles, bathroom floor tiles, kitchen tiles, sinks and enamelware, generally, without harming the surfaces thereof. It is recognized that many of such surfaces are acid-resistant but a commercial product must be capable of being used without harm on even less resistant surfaces, such as European enamel (often on a cast iron or sheet steel base) which is sometimes referred to as zirconium white powder enamel. It is a feature of the cleaner described above (and other cleaners of this invention) that they clean hard surfaces effectively but they do contain ionizable acids and therefore should not be applied to acid-sensitive surfaces. Nevertheless, it has been found that they do not harm European white enamel bathtubs, in this example, which are seriously affected by cleaning with preparations exactly like that of this example except for the omission from them of the phosphonic acid or the phosphoric-phosphoric acid mixture.

## Claims

1. An acidic microemulsion hard surface cleaner composition which has a pH in the range of 1 to 4 which removes lime scale, soap scum and greasy soil from hard surfaces characterised in that it comprises a detergent proportion of synthetic organic detergent, which is capable of removing greasy soil from such surfaces; a lime scale and soap scum removing proportion of an alpha hydroxy aliphatic acid, an aminoalkylenephosphonic acid, water and a perfume.
2. A composition as claimed in claim 1 characterised in that the said alpha hydroxy aliphatic acid has 2 to 6 carbon atoms.
3. A composition as claimed in claim 1 or claim 2 characterised in that the aminoalkylenephosphonic acid contains 1 to 3 amino nitrogen(s), 3 or 4 lower alkylenephosphonic acid groups and 0 to 2 lower alkylene groups of 2 to 6 carbon atoms each, which alkylene(s) is/are present and connect(s) amino nitrogen when a plurality of such nitrogen is present in the aminoalkylenephosphonic acid.
4. A composition as claimed in claim 1, 2 or 3 characterised in that the ratio of the said alpha hydroxy aliphatic acid to the said aminoalkylenephosphonic acid is in the range of 5:1 to 250:1.
5. A composition as claimed in claim 1, 2, 3 or 4 characterised in that the synthetic organic detergent is a C<sub>8-18</sub> alkyl sulphate surfactant.
6. A composition as claimed in anyone of claims 1 to 5 characterised in that there is also present phosphoric acid which improves the action of the aminoalkylenephosphonic acid in protecting zirconium white enamel surfaces of items being cleaned against the action of the alpha hydroxy aliphatic acid(s).
7. A composition as claimed in claim 6 characterised in that the proportion of phosphoric acid is in the range of 2:1 to 10:1 with respect to the aminoalkylenephosphonic acid and the ratio of alpha hydroxy aliphatic acid to the phosphoric acid is in the range of 5:2 to 25:1.
8. A composition as claimed in claim 7 characterised in that it comprises 1 to 9% of the synthetic organic anionic detergent(s), 1 to 6% of synthetic organic anionic detergent, 2 to 9% of the alpha hydroxy aliphatic acid, 0.05 to 1% of the phosphoric acid and 0.01 to 0.3% of the aminoalkylenephosphonic acid(s).
9. A composition as claimed in anyone of claims 1 to 8 characterised in that the said alpha hydroxy aliphatic acid is a mixture of malic acid and lactic acid.
10. A composition as claimed in anyone of claims 1 to 8 characterised in that the said alpha hydroxy aliphatic acid is a citric acid.